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Project Reports (4)

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DIFFERENTIAL THERMAL STUDIES OF CLAY-STARCH FILMS

INTRODUCTION

The efficiency of an adhesive as a binder for pigments in the coating of paper and paperboard is a function of many variables including the manner in which the material is adsorbed at the pigment surfaces (1). These surfaces provide a unique chemical environment that may influence the properties of the absorbed adhesive. Failure of an adhesive bond rarely occurs at the adherend-adsorbant interface (1, 2, 3); therefore the properties of the adsorbed bonding material and their contribution to cohesive strength in the boundary layers near the interface are of importance. The writer has proposed that adsorption of an adhesive such as starch on the surfaces of pigments, and on kaolin clay in particular, could cause a change in the properties of the starch from those properties observed in a free film.

It is suggested that the adsorption of starch layers by the clay would be with such energy levels that a higher temperature would be required to decompose the adsorbed starch than similar nonadsorbed starch. The clay would therefore be responsible for holding starch tightly and perhaps the first few adsorbed layers would be held most tightly. These starch layers could even possess a unique crystalline form in the region of this clay-adhesive interface. The interfacial properties at this junction are considered to be of particular importance. The work reported herein is concerned with the thermal decomposition of starch in the presence of clay.

The original concept for which the differential thermal analyses (D.T.A.) were made on the clay-starch systems in this study was quite simple. If starch alone gave a good differential thermal characterizing curve, it should also show the same characteristic thermal decomposition in the presence of another material, such as clay, if no interaction was present. Clay (kaolin) has an initial decomposition temperature of about 525-550°C. (5) whereas starch has a thermal breakdown beginning at about 250-260°C. (6). If the clay has an influence on the properties of the starch, the effect could be evident since the two temperature changes are quite different and are widely separated on the D.T.A. chart.

During the spring and summer months of 1964, preliminary studies were made of differential thermal analysis (D.T.A.) techniques. The equipment used was the Du Pont 900 D.T.A. apparatus on loan from the Du Pont Company. The brief study described here is only introductory as to the experimental procedures and interpretations that are potentially possible with this type of equipment.

EXPERIMENTAL

The theory proposed above was studied using pigment coating films prepared from colors containing Special Hydratex Clay (kaolin clay from the J. M. Huber Corporation) and Superfilm 40 (hypochlorite oxidized starch from Stein-Hall & Company, Inc.) as the adhesive. The clay was dispersed to a minimum viscosity at 72% solids and at pH 7.5 using 3 meq. of Quadrafos per 100 grams of clay as the dispersing agent. The starch was cooked in a Corn Industries Research Foundation viscometer for 30

minutes at 95°C. The adhesive slurry was added to clay in amounts equal to 2, 4, 8, 12, 16, and 20% starch based on the weight of the clay.

The final coating colors were formulated at 55% total solids and allowed to condition for three hours at 73°F. Films of each color were formed on glass using a Bird drawdown bar to spread the film. The films were air dried at 50% relative humidity and then scraped from the glass surface with a razor blade forming a powder for further test.

The powders of the samples to be tested were packed into macro-thermal cells and heated at a rate of 30°C. per minute in the Du Pont 900 Differential Thermal Analyzer using glass beads as the reference standard. In the studies of kaolin clay alone, calcined alumina was used as the reference standard. The differential temperatures were plotted on the instrument recorder and the ΔT curves corrected for scale shifts. The recorded temperatures were corrected for the chromel-alumel thermocouple calculated from calibration curves supplied with the instrument.

Initial decomposition temperatures were obtained from the D.T.A. curves by determining the intersection of the slope of the background line joining the shoulders of an endotherm dip and the extension of the most linear part of the low temperature side of the dip in the curve as suggested by Vassallo and Harden (7). The final decomposition temperature was taken as that temperature represented by the minimum point in the endotherm. Interpretations were made in the temperature ranges of 225-325°C. for starch and 500-600°C. for the clay. The low temperature endotherms in the range of 90-120°C. are normally attributed to the loss of free or uncombined water present in these systems.

The reproducibility of the D. T. curves was not as good as desired due to a lack of experience and familiarity with the equipment as well as needed refinements in the techniques of sample preparation. Therefore, at present, there is a limitation to the reliability in the interpretations of these data. However, the results for the duplication and series sequence that were obtained with the equipment gave a fairly good idea of what potentially can be expected from such procedures.

RESULTS AND DISCUSSION

STARCH-CLAY STUDIES

The data obtained from the D.T.A. studes on starch-clay films are given in Table I and the characteristic thermal curves are shown in Figure 1. These data indicate that the initial decomposition temperature of starch was increased in the presence of clay. This value remained greater than 270-280°C. until 16% starch was present. Above this level, the initial decomposition temperature dropped to 245°C. and the minimum point in the endothermic portion of the curve was 285-295°C., rather than 295-315°C. The temperature shift in this range appears to be significant and several layers of the starch are apparently involved.

TABLE I

EFFECT OF CLAY PIGMENT ON DECOMPOSITION TEMPERATURE OF STARCH
(Presumably adsorbed)

Starch Added, %	Test Environment	Low Temp., Minimum	D.T.A. Points, °C. Initial Peak	D.T.A. Points, °C. Peak Minimum
0	Air	--	--	--
2	"	--	--	--
4	"	?	270	305
8	"	120	284	305
"	"	110	290	312
12	"	132	270	305
16	"	122	271	307
"	"	120	289	313
"	"	132	275	301 (?)
20	"	123	246	295
Starch	Air	122	245	293
"	N_2	117	266	286
"	N_2	--	249	289

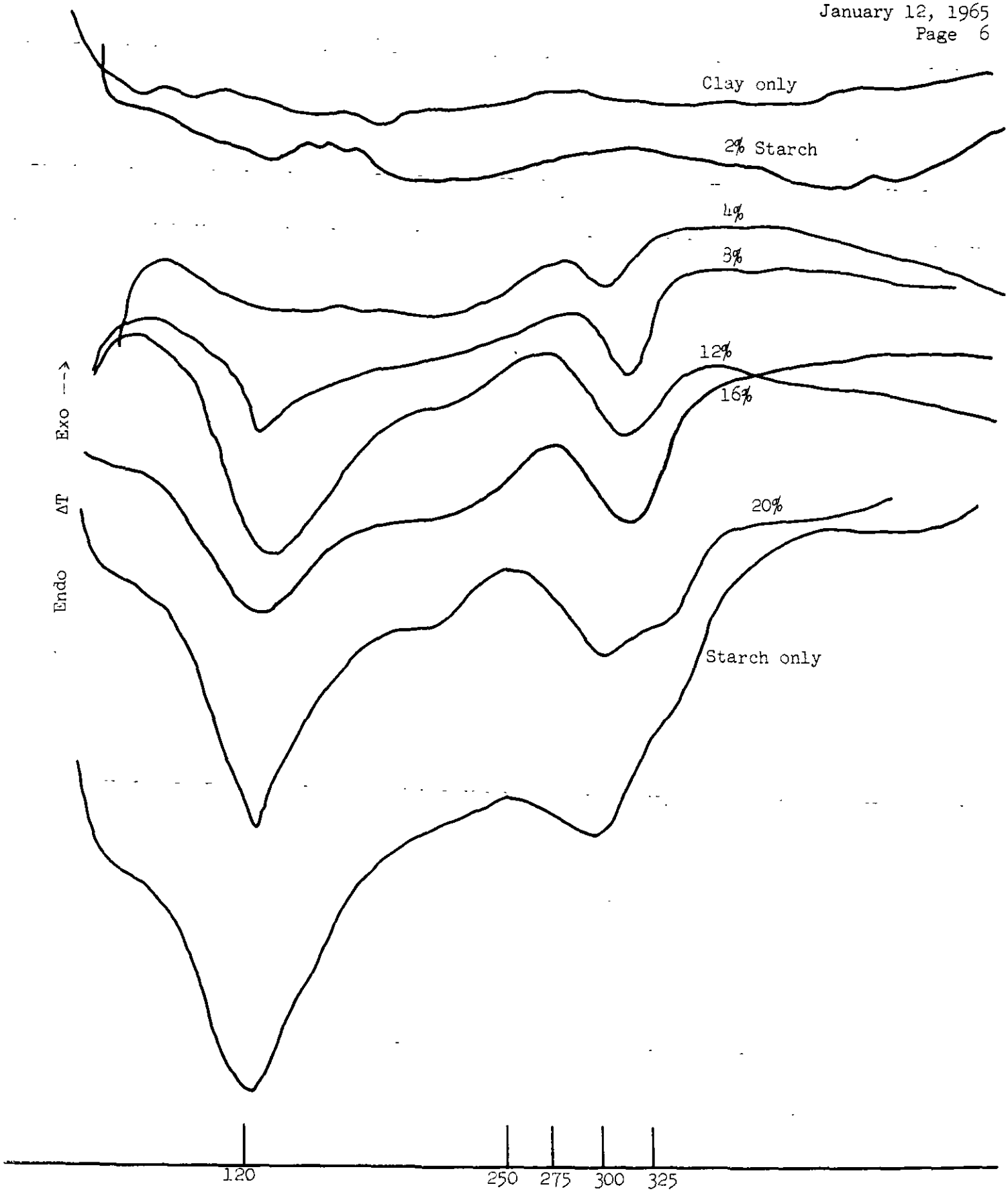

Figure 1. Differential Thermal Curves of Starch-Clay Films

It is of interest to note that 16-17% starch based on clay is a level considered to have adequate bonding strength with this clay coating system on paper. This amount of starch is probably more than enough to cover the surface of the clay with a single "monolayer" of starch. The concept of a monolayer of starch in this system is not good, and, in binding of pigments in coatings, the adhesive may, but does not necessarily, cover all surfaces. The data from Cobb (4) can be calculated to show that a "monolayer" of casein on clay is achieved at only 1% casein by weight. The thickness dimension of an amylopectin unit for starch is uncertain and, due to the bulk properties in the branched starch polymer, any concept of a starch "monolayer" is difficult to visualize.

The amount of starch required for such a layer must therefore be more than for casein--perhaps requiring 3-4% by weight. If this is correct, 8% starch would give two layers, and 16% approximately four layers. It is known that adsorption forces are reduced rapidly with distance and further layers may not be visualized.

Cobb (4) further points out that a monolayer concept is not in keeping with modern ideas of bonding. Therefore, the number of layers influenced in the studies discussed herein must be more than four and the influence of the clay on the starch is probably structural orientation of the polymer as well as direct polymer adsorption.

The endothermic portion of the D.T.A. curves at 50-120°C. in Figure 1 shows an increase in area with an increase in the amount of starch present with the clay. The endothermic reaction is related to the water content of such systems and under carefully controlled conditions is a useful criterion(8). This area is a function of the release of free water and water that is present in the retrograded starch form. There is, however, no change in the temperature at the minimum point in this portion of the diagram.

These experiments on the D.T.A. of starch in presence of clay are worthy of additional work. The series of clay-starch adsorption interactions should be repeated with considerably more control over the conditions of sample preparation, conditions of test, weighing of sample in place of packing the test vial by volume, etc., in order to obtain more precision. More samples could be evaluated, especially between 12 and 20% starch and more reproducibility is required.

These experiments also indicate a need for an expansion of the study using other types of starch as the adhesive with clay. It is visualized that proteins and polyvinyl alcohol may have properties that can be studied by D.T.A. methods as well as resins that may be used as emulsions in coatings such as styrene-butadiene, acrylics, etc. It is suggested that if the adsorption of the adhesive would not cause a change in the thermal decomposition of D.T.A., no bonding or only weak bonding would occur.

CLAY STUDIES

The D.T.A. studies also included a comparison of dispersed and nondispersed clays and these results are given in Table II and Figure 2. The clay that was not predispersed had a temperature of about 590°C. at the minimum point in the endothermic curve for decomposition. However, the minimum point in this region for predispersed clay was found to occur at 600°C. The evaluation of the extrapolated shoulder of the decomposition curve was also higher for the predispersed clay than for clay that had not been predispersed. The determination in an atmosphere of nitrogen did not affect these results. The main features of these curves agree well with the summaries provided by Brown (5) but his works did not discuss dispersion effects.

It should be noted that in the case of the clay-starch studies where the clay was dispersed in the laboratory, the effect of dispersion on clay was also recorded as shown in Table II. Whether or not the differences observed are actually an effect of particle size resulting from the use of the polyphosphate dispersing agent has not been checked at this time. The explanations for the results obtained on these dispersed clays at present are uncertain and more studies must be made in this area.

TABLE II

EFFECT OF STATE OF CLAY DISPERSION ON DECOMPOSITION TEMPERATURE OF THE CLAY

Clay Identification	Test Condition: Environment	Test Condition: Cell Size	D.T.A. Points, °C.: Nondispersed - Break	Nondispersed - Peak	Predispersed - Break	Predispersed - Peak
H T Coating	Air	Macro	551	590	556	600
Hydratex	Air	Macro	550	590	565	600
"	"	"	551	590	565	600
"	"	"	--	--	561	601
"	"	Micro	--	--	567	600
"	N_2	Macro	550	590	--	--
Clay + starch (8%)	Air	Macro	551	593	(but lab.dispersed)	
" " (16%)	"	"	565	598	" "	"
" " (16%)	"	"	561	598	" "	"

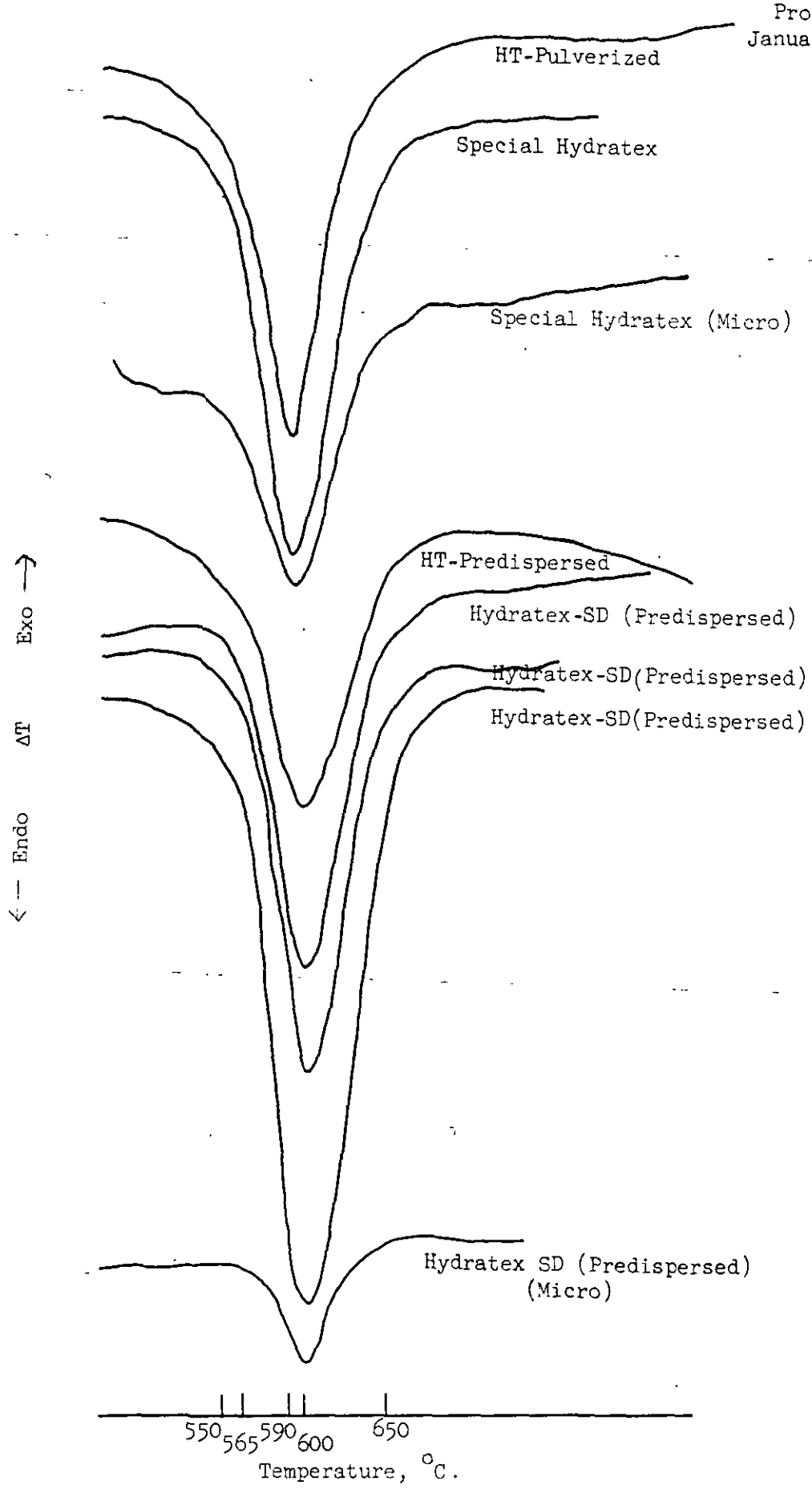

Figure 2. Differential Thermal Curves of Nonpredispersed and Predispersed Clays

DISCUSSION

Based on the information obtained in these studies, additional work on both starch-clay systems and dispersed clay systems is highly recommended. These techniques together with additional information obtained from an infrared procedure and the usual laboratory techniques could contribute significantly to the knowledge and understanding of coating behavior. The real manner in which the coating components contribute to the coating properties is not as well understood as they should be using the techniques that are potentially available.

SUMMARY

Differential thermal analysis (D.T.A.) can be used to qualitatively and perhaps quantitatively identify starch in the presence of clay.

D.T.A. shows that adsorbed starch on clay probably has a higher decomposition temperature than does nonadsorbed starch found in a free film. A level of 16% starch based on the weight of clay is required before the effect of clay on the thermal decomposition of adsorbed starch can no longer be detected.

D.T.A. indicates higher decomposition temperatures for dispersed than for nondispersed kaolin clay (contains polyphosphate).

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ORIENTATION STUDIES

CRYSTAL STRUCTURE OF $ZnCl_2 \cdot C_6H_5CHO$

The Weissenberg camera which was received recently has been placed in routine operating order for the study of single crystals. An appropriate slit system has been developed for the x-ray tube, the camera has been aligned with respect to the x-ray tube, and numerous single crystal rotation photographs and Weisseenberg photographs have been taken.

The crystal used for the above photographs was a benzaldehyde-$ZnCl_2$ complex reported by Dorcheus and Williams (1). The reasons for chosing the complex are that it was available from previous work at The Institute of Paper Chemistry, it is an interesting chemical problem involving a metal-carbonyl complex in which the carbonyl group is linked to an aromatic system, it has a potential role in the benzylidation of glucose, little structural work has been completed on $ZnCl_2$ complexes, and the chemistry involving the zinc ion is of importance in the vulcanization of cellulose.

Rotation photographs were recorded with the crystal aligned about all three of its axes. Layers zero through two were recorded with the crystal aligned about the b axis and layer zero was obtained with the crystal aligned about the a axis. The following information was derived

from the above photographs. The benzaldehyde $ZnCl_2$ complex has monoclinic symmetry with cell dimensions $a = 4.8$ Å, $b = 5.6$ Å, and $c = 21.5$ Å and the monoclinic angle $\beta = 98^{\circ}$. Assuming 4 molecules are contained in the unit cell, the crystallographic density is approximately 2.6 g./cm.^{3}. For the hol data a reflection appears only if l is an even integer and for the oko data a reflection is observed only if k is an even integer. These conditions for the existence of a reflection indicate that the crystal has the unique and centrosymmetric space group $P2_1/c$.

The crystals used for this work were rectangular platelets approximately .02 mm. thick. The longest edge of the crystal as seen under the microscope corresponds to the b axis while the short length of the platelet corresponds to the c axis. Neither of the crystals used to obtain the data decomposed in the short period required for the photographs, although some decomposition was apparent after a couple of days. In future work where a long exposure to the atmosphere is necessary it would be best to coat the crystal with a suitable material or seal the crystal in a capillary. No effort was made to choose ideally shaped crystals. Any future experiments would require a more careful selection and shaping of the crystal.

Since this crystal contains a heavy zinc atom and two chlorine atoms of intermediate atomic number, this structure could be solved by conventional heavy atom techniques. The shape and size of the unit cell along with the centrosymmetric space group make this problem quite favorable for structural studies. A good set of intensity data would be

required. This would necessitate careful preparation and selection of a crystal and the recording of intensity photographs. The quality of the data would be better if these photographs were recorded at low temperatures.

This research carried out under Project 1102-8 illustrates the amount of information which can be obtained with a minimum of time using the camera which was recently purchased for the Physical Chemistry Section.

It is recommended that this investigation, which was initiated and surveyed under Project 1102-8, be continued under an institutional project over the coming months with a time allotment commensurate with other co-operative and institutional projects being carried on at this time.

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SIGNED Norman L. Colson

Norman L. Colson

A PRELIMINARY EVALUATION OF INDIAN GUAR GUM, CYANOSIZE 400, AND SCOTCHBAN FX-806 AS BEATER ADDITIVES

SUMMARY

A preliminary evaluation was made of Indian guar gum as a beater adhesive and of Cyanosize 400 and Scotchban FX806 as internal sizing agents in paper. More specifically, Cyanosize was tested as a sizing agent for water resistance; FX-806 as a sizing agent for oil resistance.

The guar gum was incorporated in lightly beaten bleached softwood pulp at 0.5 and 2.0% addition levels in the presence of, and in the absence of, rosin-alum size. Domestic guar gum (Lycoid OPMC) was employed as a reference beater adhesive.

Scotchban FX-806 and Cyanosize 400 were incorporated into the same pulp at the 0.2 and 0.5% addition levels at pH 7. Aquapel 364 was used for reference purposes under the same conditions.

Physical test results on the handsheets revealed that, on an average, the Indian guar gum was as effective as domestic guar gum in improving strength properties.

Scotchban FX-806 produced a low level of oil resistance, and Cyanosize 400 failed to provide measureable water resistance under the conditions used in these experiments.

INTRODUCTION

This is Project Report 16 on Project 1102-8. The present report is concerned with the evaluation of Indian guar gum as a beater adhesive, and Cyanosize 400 and Scotchban FX-806 as sizing agents for paper.

The samples of Indian guar gum was provided by Mr. P. D. Khandor of DAVARS M. P. Food Products, Gwalier, India. Cyanosize 400 is a product of American Cyanmid and is advocated for the alkaline sizing of paper and board. FX-806 is marketed by the Minnesota Mining and Manufacturing Company as an internal additive for improving oil and grease resistance.

It is pointed out that rather routine evaluation techniques were utilized in these experiments which may not have been to the best advantage of the products involved.

EXPERIMENTAL

PREPARATION OF ADDITIVES

Indian guar gum (9.4% predetermined solids) and Lycoid CPMC (commercial grade of guar gum) were dispersed at 0.5% solids for addition to the pulp. A 2.0-gram (O.D. basis) aliquot of gum powder was sprinkled into well-agitated, room temperature distilled water contained in a 500-ml. Erlenmeyer flask (total weight of water and gum = 400 grams). The 0.5% dispersion was cooked at 90-95°C. over steam for 30 minutes with high speed agitation provided by a Lightnin' mixer. Prior to addition to the pulp, the cooked gum was cooled to 25°C.

The viscosity of the cooked 0.5% Indian guar gum was measured on the Brookfield Model LVF Viscometer at 72°F. employing Spindle No. 2. The viscosity ranged 65 to 75 cps. at 60 to 6 r.p.m., respectively. (Note: Because of insufficient sample volume to use Spindle No. 1, Spindle No. 2 was employed.)

Scotchban FX-806 was received at 30% solids. Prior to use in sheetmaking, a 1.5-g. aliquot was diluted to 1.5% solids with room temperature distilled water.

Cyanosize 400 was received at 14.2% solids; prior to addition to pulp a 3.17-g. aliquot was diluted to 1.5% solids with room temperature distilled water.

Aquapel 364 (Hercules) was obtained from the Fox River Paper Corpration in emulsified form at 3.3% solids. Until used in handsheet preparation, the emulsion was kept refrigerated.

Cationic (Cato-8) starch was cooked at 2.0% solids in distilled water for 30 minutes at 90-95°C. over steam. Following the cooking cycle, the starch dispersion was cooled to 25°C. for addition to the pulp.

Hercules Powder Company's Pale Rosin Size was dispersed at approximately 4% solids in warm distilled water.

Reagent-grade aluminum sulfate [$Al_2(SO_4)_3 \cdot 18\ H_2O$] was prepared as a 10% solution in distilled water.

Sulfuric acid, employed for pH adjustments, was prepared by diluting 30 ml. of concentrated (H_2SO_4) to a total volume of 1500 ml. with distilled water.

PROCESSING OF PULP

Weyerhaeuser bleached sulfite pulp was processed for sheetmaking by beating in tap water at pH 7 in a Valley beater. There were three beater charges refined to a combined 690 cc. Schopper-Riegler freeness and a resulting 1.45% consistency.

HANDSHEET PREPARATIONS

Aliquots of the refined 1.45% consistency pulp, sufficient to prepare a set of handsheets (4 to 8 sheets of 2.5 g. each) were metered into 3-liter stainless steel beakers. Guar gums (Indian and Lycoid OPMC) were incorporated into the pulp at 0.5 and 2.0% addition levels (based on O.D. fiber) both in the presence and absence of rosin size and alum.

Scotchban FX-806, Cyanosize 400, and Aquapel 364 were incorporated into the pulp at 0.2 and 0.5% addition levels (based on O.D. fiber). Cationic starch (Cato-8) was employed in conjunction to Aquapel. The Cato-8 starch was added after the Aquapel had been stirred in. Contact times of 15 minutes were employed for all additives except Cato-8 starch, rosin and alum for which contact times of 5 minutes were employed. In those sets of sheets where rosin and alum were employed, the beater adhesives were stirred in contact with the pulp for 15 minutes after which 2% of rosin (based on fiber) was added and allowed to stir in for 5 minutes. The rosin was followed by the addition of 4% of papermakers' alum which was sufficient to lower the pH to 4.5-5.0. After stirring for an additional 5 minutes the furnish was diluted to 0.5% consistency.

In the absence of rosin and alum, the pH of the pulp slurry was adjusted to 7.0, after diluting to 0.5% consistency and maintained at that level throughout the sheetmaking process by the addition of 2% sulfuric acid.

The handsheets were formed on an 8 by 8-inch Noble & Wood sheet mold, employing a 100-mesh monel wire, at a consistency of 0.04% in filtered tap water. In the case of the rosin-sized sheets the pH in the sheet mold was maintained at 4.5-5.0 by the addition of 2% sulfuric acid. After forming, the handsheets were couched onto blotters, pressed between blotters for five minutes at a 50 p.s.i. gage reading in the Valley press. All handsheets were dried for 7 minutes on a steam drum at 3-1/2 lb. of steam pressure (220-230°F.).

PHYSICAL TESTS

Handsheets containing the guar gums (Indian guar and Lycoid OPMC) plus control sheets were tested for the following: Basis weight, caliper, apparent density, bursting strength, tensile, tear, tear factor, and M.I.T. fold.

The handsheet sets containing Scotchban FX-806, Cyanosize 400, Aquapel 364, plus Cato-8 and blank controls were tested for the following: Basis weight, caliper apparent density, and fluorescence size.

Handsheets containing Scotchban FX-806 and/or Aquapel were examined for surface oil resistance employing the 3-M Surface Oil Resistance Kit Test. The kit is made of a graded series of twelve solutions containing castor oil, toluene, and heptane; the higher the kit number the greater the proportion of solvent and hence, the greater the penetrating power. Therefore, in testing paper the higher the kit number the better is the oil resistance. Test results for all the handsheets are listed in Table I.

TABLE I

EVALUATION OF INDIAN GUAR GUM, FX-806, AND CYANOSIZE IN BLEACHED SULFITE PULP

Handsheet Set No.	Additives, % (Based on fiber)	Basis Wt., 25x40/500	Caliper, mils	Apparent Density	Burst Strength pts.	Burst Strength pts./100 lb.	Tensile, lb./in.	Tear, g./sheet	Tear Factor	M.I.T. Fold (Double Folds)	Fluores. Size, sec.	MMM Kit Test
			Nonrosin-Sized Sheets--pH 7									
1	Blank controls	46.1	4.3	10.7	34.8	75	19.8	55	1.19	324	Instant.	--
2	Lycoid OPMC, 0.5	46.0	4.3	10.7	43.0	94	21.7	47	1.02	595	--	--
3	Lycoid OPMC, 2.0	45.3	4.2	10.8	46.6	103	22.1	42	0.93	744	--	--
4	Indian guar gum, 0.5	44.7	4.2	10.6	41.2	92	22.1	43	0.96	657	--	--
5	Indian guar gum, 2.0	45.5	4.2	10.8	46.4	102	22.9	42	0.92	867	--	--
			Rosin-alum-Sized (2% rosin, 4% alum) - pH 4.5-5.0									
6	Rosin-alum controls	45.9	4.4	10.4	33.9	74	17.4	55	1.20	150	48	--
7	Lycoid OPMC, 0.5	46.0	4.3	10.7	39.4	86	20.6	52	1.13	440	--	--
8	Lycoid OPMC, 2.0	45.3	4.2	10.8	43.4	96	22.1	44	0.97	680	--	--
9	Indian guar gum, 0.5	45.0	4.3	10.5	37.8	84	20.0	47	1.04	352	--	--
10	Indian guar gum, 2.0	44.6	4.3	10.4	42.1	94	21.6	44	0.99	591	--	--
			Sets Prepared at pH 7									
11	Aquapel, 0.2 + Cato 8, 0.3	44.2	4.3	10.3	--	--	--	--	--	--	42	--
12	Aquapel, 0.5 + Cato 8, 0.75	44.8	4.2	10.7	--	--	--	--	--	--	58	--
13	FX-806, 0.2	44.9	4.3	10.4	--	--	--	--	--	--	Instant.	1
14	FX-806, 0.5	45.9	4.5	10.2	--	--	--	--	--	--	Instant.	3
15	Cyanosize 400, 0.2	45.0	4.3	10.5	--	--	--	--	--	--	Instant.	--
16	Cyanosize 400, 0.5	44.2	4.3	10.3	--	--	--	--	--	--	Instant.	--

DISCUSSION OF RESULTS

The results indicate that Indian guar gum is roughly comparable to domestic guar in strength development.

With respect to unsized paper, the 0.5% addition of the guar products produced strength improvements amounting to 22-25% in burst and 9-11% in tensile. The improvements were increased to 36-37% in burst and 11-16% in tensile at the 2% addition level.

In rosin-sized paper the strength improvements attained at the 0.5% addition level amounted to 13-16% in burst and 15-18% in tensile. These advantages were increased to 27-30% in burst and 24-27% in tensile at the 2% level.

Some differences in the effectiveness of the two guar products are indicated in the fold test results, but these may not be significant considering the variability normally encountered in this test.

Of the internal sizing agents tested, only the reference agent (Aquapel) provided water resistance. Scotchban FX-806 provided some oil resistance but the level attained would not be considered adequate for most applications requiring that property.

Again it is pointed out that the conditions used in these screening experiments may not have been favorable to the particular sizing agents tested. Additional testing would be required for a more complete analysis.

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STUDIES ON METAL-CARBOHYDRATE COMPLEXES

INTRODUCTION

Many of the chemical systems which are of great importance to the paper industry are systems which are not purely organic in nature but consist of cellulose or other organic materials in contact with metal ions. Examples of such systems would be the vulcanization of cellulose, dissolving of cellulose, and sizing systems for paper. Here the ions of Zn, Fe, Cu, and Al influence the properties of the systems. The hydroxyl groups on the polyhydroxy compounds are available for some type of interaction with the metal ions. In some cases two hydroxyl groups may become oriented such that a metal ion can co-ordinate to both hydroxyls forming a ring.

An example of the influence of a salt on the behavior of a polysaccharide is given by the reaction of certain linear polysaccharides with iodine in a 30% solution of calcium chloride (1). In the presence of $CaCl_2$ the iodine complexes with the polysaccharides, but no reaction occurs without the $CaCl_2$.

With the immense importance of these polyhydroxy compounds in industry, in the biological activity of animals, and in plant life (chemical systems which require certain metal ions) it is disappointing to observe that little research has been carried out on the preparation and study of these compounds co-ordinated to metals. However, the organic chemistry

of the simple sugars has been studied in detail.

Some compounds formed by the reaction of $CaCl_2$ with the simple sugars have been reported. The first $CaCl_2$ sugar compounds to be reported were with D-mannose (2, 3,). These compounds had the composition mannose. $CaCl_2 \cdot 4H_2O$ and mannose $\cdot CaCl_2 \cdot 2H_2O$. The compound containing $4H_2O$ was crystallized from water, while the compound with $2H_2O$ was crystallized from an alcohol solution. From polarimetry studies it was suggested that the conformation of mannose was different in the two mannose.$CaCl_2$ complexes(2). In water solution association between the $CaCl_2$ and mannose existed, even on dilution.

After the preparation of the D-mannose.$CaCl_2$ compounds, several other sugars were reacted with $CaCl_2$. The sugars that formed complexes with $CaCl_2$ were ⍺-D-gulose (4, 5), D(-)arabinose (6, 7), and D(+)xylose (8). There is also some evidence that D-fructose, D(+)-galactose, and sucrose form similar compounds. The ⍺-D-gulose.$CaCL_2 \cdot H_2O$ has been used to prepare other derivatives of gulose (9, 10) and was the first crystalline product isolated from gulose. Pure ⍺-D-gulose is known only in the form of a syrup.

Both $Zn(OH)_2$ (11) and $Cu(OH_2)$ (12) have been reported to form compounds with the simple sugars. These compounds were not crystalline. Aluminum has formed compounds with some Cis-Methoxycyclohexanols (13) by means of a lithium aluminum hydride-aluminum chloride reagent in an organic solvent.

In an effort to gain insight into this area of research some work has been started under Project 1102-8. Attempts were made to prepare the

calcium chloride compounds, prepare some new compounds with different metals, and to observe the nature of these compounds (ease of preparation, stability, and crystallinity) with the hope of finding suitable crystals for future x-ray analysis. One problem with x-ray structural studies of pure sugars is the difficulty in obtaining good single crystals of a suitable size.

PREPARATIONS AND X-RAY DATA

Attempts were made to prepare the $CaCl_2$ derivatives of the following sugars: dextrose, sucrose, D(+) galactose, D-mannose, D(+)xylose, D(-)arabinose, cellobiose, and xylobiose. These preparations were made by evaporating a water solution of $CaCl_2.2H_2O$ and the sugar (mixed in a one to one molecular ratio) under vacuum until a syrup was obtained. In the case of D-mannose, D(+)xylose, D(-)arabinose, and xylobiose, crystals formed immediately. The other syrups haven't yielded crystals. The following chemical and crystal information was obtained from these compounds:

D-mannose $CaCl_2.4H_2O$--Crystals appeared in the syrup formed by the calcium chloride-mannose mixture after standing two days in a round bottom flask at room temperature and pressure. The crystals were rhombic in shape, thin, and quite hydroscopic. A dry box was built to handle the crystals, and a dry atmosphere was mainained around the microscope while crystals were being mounted in capillaries for x-ray examination. Three layers of Weissenberg data and some rotation data were recorded along one of the axes. The rotation axis had the length 9.7 Å with the other two dimensions being 12.2 Å and 9.5 Å. The crystal appears to be in the monoclinic system with possible space groups C2,

[redacted] or Cc. This size cell would only facilitate two molecules per unit cell.

D(+)xylose $CaCl_2.3H_2O$ -- This compound crystallized immediately after the water was removed from $CaCl_2$-xylose mixture by means of a rotary evaporator. Large rhombic shaped crystals could be obtained easily, both from a water solution and an alcoholic solution. The crystals were quite stable. On one occasion the crystals stood for several hours on a glass slide with a minimum of decomposition. From the x-ray data obtained the unit cell appears to be monoclinic with cell dimensions of 12.9, 14.8, and 7.8 Å. The calculated density is 1.39 g./cm.^{3} if the cell contains four molecules. The measured density is 1.48 g./cm.^{3}.

Xylobiose.$CaCl_2.XH_2O$ -- Approximately one gram of impure xylobiose and three grams of $CaCl_2.2H_2O$ were dissolved in water. This solution was concentrated on a rotary evaporator until crystals appeared. Because of the impurity of the xylobiose, no attempt was made to characterize the crystals. It appeared that the xylobiose that was present formed a crystalline compound with the $CaCl_2.2H_2O$.

In a manner similar to the $CaCl_2$.sugar preparation, attempts were made to then prepare some $AlCl_3$.sugar complexes. The same simple sugars were used as in the calcium chloride case. Equal molar amounts of $AlCl_3.6H_2O$ and the sugar were dissolved in water and evaporated on a rotary evaporator. In all cases a crystalline precipitate was obtained. The precipitate was studied carefully by removing crystals and taking x-ray patterns. The crystals studied

were those of $AlCl_3.6H_2O$. It appears that the $AlCl_3.6H_2O$ did not complex with the sugars. The $AlCl_3$-carbohydrate system would probably justify some more study.

No crystal formation was observed when a water solution of $FeCl_3$ and D(-) arabinose was concentrated on a rotary evaporator. A dark syrup was obtained. $CuCl_2$ was mixed in a one to one molecular ratio with several sugars including D(+)xylose dextrose and D(+) galactose. These mixtures were dissolved in water and concentrated on a rotary evaporator until fine needlelike crystals appeared. Separating the crystals from the syrup was difficult, but it appeared that a very hydroscopic crystalline compound formed between $CuCl_2.2H_2O$ and the carbohydrates.

There are a group of compounds that can be prepared by the reaction of $Cu(OH)_2$ and carbohydrates (12). Some of these compounds were prepared, and they were found to be noncrystalline solids unsuitable for x-ray diffraction studies.

One of the primary difficulties in forming complexes with the sugars is finding suitable solvent systems. Solvents which are not polar do not dissolve the simple sugars. The more polar solvents which dissolve the sugar may compete with the sugar for the co-ordination to the metal atom.

CONCLUSIONS

From the work completed heretn Project 1102-8 several possibilities exist for future research:

(1) Encouragement should be extended to chemists interested in the preparative aspects of these complexes. In the future model systems can perhaps be developed for studying important problems of interest to the paper industry.

(2) Mannose is believed to be in the furanose form in the D-mannose.$CaCl_2$.$4H_2O$ compound. This feature of the sugar along with the nature of its co-ordination to metal in the complex makes this a good crystal structure problem. No compound involving Ca co-ordinated to a polyhydroxy compound has been studied in detail.

(3) D(+)xylose.$CaCl_2$.$3H_2O$ forms a very stable crystal of good shape and size. The stability of this complex is quite intriguing. Its ease of handling and crystal data make it a likely prospect for structure studies.

(4) An extremely interesting complex to study would be α-D-gulose.$CaCl_2$.H_2O. There is a great deal of confusion on the conformation of α-D-gulose and its derivatives both in solution and the solid state. Recent work by infrared and N.M.R. spectroscopy fail to give conclusive evidence on the conformation of the pyranose ring.

(5) A complex between xylobiose and calcium chloride would provide a good opportunity for studying the structure of xylobiose. A completed structure of this complex would be very helpful in understanding the chemistry of polysaccharide systems.

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The Institute of Paper Chemistry

MEMORANDUM

From R. M. Leekley

To Mr. W. Smith

Date April 5, 1966

Subject Project 1102-8; Report 17

This report number was assigned to us to cover material which I have since decided should not be written up as a report. Therefore, final typing of the report was never completed. Please consider Report 17 as cancelled.

Since Report 18 has been issued and circulated, this should be the easiest way to handle this matter inasmuch as we should have a record of this in our files.

RML/mce

FORM 8-3-A
10,000—3-65

PROJECT REPORT FORM

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G. F. Richards
Dale G. Williams
Reading Copy

PROJECT NO. 1102-8
COOPERATOR Inst. of Paper Chemistry
REPORT NO. 19
DATE April 7, 1966
NOTE BOOK 1678:66-70, 72, 79, 136-9
PAGE " 670: ~~xx~~ p. 135-6
SIGNED Dale G. Williams
Dale G. Williams

CRYSTALLOGRAPHIC DATA OF SOME CARBOHYDRATES

SUMMARY

Structure determinations of the lower members of the cellodextrins are a direct way of determining the structure of Cellulose II and ultimately Cellulose I. As an initial step in this structure work, attempts were made to prepare suitable crystals of cellotriose, cellotetraose, and cellopentaose by slow crystallization of the small amounts of these materials available. The attempts were not successful and it is felt that greater quantities of pure materials are needed.

A survey of x-ray diffraction data was made of methyl-β-glucoside, methyl-β-cellobioside, D-galacturonic acid, and β-D-mannose. The first two compounds are often used as model compounds for cellulose studies and thus knowledge of structure similarities and differences between these, their corresponding sugars, and cellulose is important. The last two compounds are structures basic to hemicelluloses and are a necessary step in their structure determination.

Suitable crystals were obtained of the first three compounds. In each case the solution of the crystal structure was found to be feasible with only one molecule in the asyymmetric unit and with the cell dimension and crystal symmetry giving a good indication of the molecular location in the unit cell. Although suitable crystals of β-D-mannose were not available,

the unit cell data in the literature indicates that this structure is also amenable to solution. These structures should be done either by thesis research or by project, the results and experience of which will be very valuable for polysaccharide structures.

INTRODUCTION

Because of the close similarity between the crystal structure of Cellulose II and that of cellotetraose and larger cellodextrins, knowledge of the cellodextrins' structures would be exceedingly useful in elucidating the detailed structure of cellulose. The purpose of this study is to survey the cellotriose, cellotetraose, and cellopentaose materials available as regards to crystallographic data (unit cells, space groups, density) ao that a specific program may be proposed for this structural objective. These materials are available in powders so that attempts to prepare crystals of sufficient size (.1 mm. dimension or larger) are necessary for the crystallographic work to proceed.

Because methyl-β-glucoside and methyl-β-cellobioside are used frequently as model compounds for cellulose and are easily obtained in single crystal form, a crystallographic survey of these was also made. In addition, a crystallographic survey was attempted for D-galacturonic acid and β-D-mannose which are potential model compounds for structure studies of hemicelluloses.

EXPERIMENTAL WORK

SINGLE CRYSTAL PREPARATION BY CRYSTALLIZATION

Cellotriose, Cellotetraose, and Cellopentaose

Slow crystallization was carried out by dissolving the small quantity (50-80 mg.) of compound in a minimum amount of distilled water at 60°C. contained in a test tube suspended in a water bath of 500 ml. volume. Propanol was added dropwise to the solution until the first traces of turbidity appeared. Water was then added dropwise until just to clarity again. The whole water bath system was then allowed to cool slowly. In spite of the care taken, the crystals formed were too small to be useful. Another solvent system or nucleation method will have to be found.

Methyl-β-Glucoside, Methyl-β-Cellobioside, D-Galacturonic Acid, and D-Mannose

Crystals of methyl-βglucoside were prepared by dissolving the material in propanol at 90°C. adding a few drops of water to the solution and allowing it to cool slowly in a water bath.

Crystals of methyl-β-cellobioside were prepared by Alan Bills by slowly cooling a hot methanol solution.

Crystals of D-galacturonic acid were prepared by dissolving the material in water at 90°C., adding propanol dropwise until turbidity, and cooling slowly in the water bath.

The one attempt to prepare D-mannose crystals by slowly cooling a hot aqueous solution to which some propanol had been added failed to yield any crystals.

CRYSTAL STRUCTURE INFORMATION FROM X-RAY DATA

Single crystals of methyl-α-glucoside and methyl-β-cellobioside were mounted on the end of glass fibers with the aid of a small amount of silicon grease. Single crystals of D-galacturonic acid were mounted and sealed inside 0.05 cm. diameter glass capillaries since these crystals appeared to decompose slowly in air.

X-ray diffraction rotation patterns were taken about each principal axis of the crystals followed in each case by x-ray diffraction, equal inclination Weissenberg patterns for the zero and the second layer. The crystal class, unit cell dimensions, and possible space groups were determined from the x-ray diffraction data. The volume of the unit cell can be used to calculate the crystal density if the number of molecules per unit cell is assumed (compatible with the symmetry operations in the space group and the assumed molecular weight) The unit cell volume may also be used to calculate the number of molecules per unit cell or molecular weight if the crystal density is known.

Methyl-β-D-Glucoside

Methyl-β-D-glucoside crystalizes as the hemihydrate (1). The crystal was found to be tetragonal, a = b = 7.3Å, c = 34.3Å , space group $P_{4_12_12}$ with Z = 8 (Z is the number of molecules per unit cell), ρ_x = 1.48, ρ_m = 1.43 (ρ_x and ρ_m refer to the density calculated from the x-ray data and to the density measured by the flotation method). This agrees with the data reported by Cox and Goodwin (2): tetragonal; a = 7.3 Å, c = 33.6 Å; $P_{4_12_12}$; Z = 8, but Werde (3) reports a measured density of 1.48. Our measured density is thus a little low.

The space group $P_{4_1 2_1 2}$ has eightfold general symmetry and fourfold special symmetry; therefore the asymmetric unit consists of one methyl-β-D-glucoside molecule in the eightfold symmetry and the water of hydration is in the special fourfold symmetry. Although this space group is noncentrosymmetric, this structure ought to be solvable with only one molecule in the asymmetric unit. The long fourfold axis (34.3 Å) means the molecule lies approximately parallel to this direction with molecule pairs bridged with a water of hydration.

Methyl-β-Cellobioside

The crystal was found to be monoclinic, a = 8.2, b = 24.3, c = 4.6 Å, and β = 112°, space group P_{2_1} or $P_{2_1/m}$, Z = 2, ρ_x = 1.45, ρ_m = 1.45. The x-ray density is based on a monohydrate since the observed density leads to a calculated molecular weight of 372, methyl-β-cellobioside $\cdot H_2O$ = 374. Space group P_{2_1} is the only space group compatible with the molecule since $P_{2_1/m}$ would require in this case that the cellobioside molecule have a mirror plane.

The asymmetric unit is one hydrate molecule which is on a screw axis in the b direction, the long axis. The major direction of the molecule, the chain direction, therefore lies approximately parallel to the b axis. The relatively short c axis (4.6 Å) is about the thickness of the puckered ring so the molecular packing is fairly well indicated. Although this space group is asymmetric, this crystal structure should be solvable, particularly with the structure of cellobiose (4) already available. The cellobioside structure would be particularly interesting because of the possible comparison of the glycosyl bond of a sugar aglycon and methyl aglycon in the same molecule. Also, the comparison of cellobioside structure with cellobiose

structure would be very informative in regards to their use as model cellulose compounds. The cellobiose structure data are not as accurate as would be desirable and would probably be worth repeating.

D-Galacturonic Acid

D-galacturonic acid crystallizes as a monohydrate. The crystal was found to be orthorhombic, a = 7.6, b = 23.8, and c = 4.9 Å, space group $P_{2_12_12}$, Z = 4, ρ_x = 1.59, ρ_m = 1.59. The asymmetric unit is one hydrated molecule and, although the space group is asymmetric, the structure should be solvable. It is particularly interesting to note, as in the case with methyl-β-cellobioside, that the dimensions of the long and short axes and crystal symmetry fairly well limit the molecular packing to the sugar ring being parallel to the b-c plane.

β-D-Mannose

Although β-D-mannose crystals were not obtained, the literature (5) reports the crystal to be orthorhombic, a = 7.62, b = 18.18, and c = 5.67, space group $P_{2_12_12_1}$, and Z = 4. As in the above cases, the asymmetric unit is one molecule and, although the space group is asymmetric, the structure should be solvable.

CONCLUSIONS

Conditions for obtaining suitable crystals of members of the cellodextrins have not yet been found. Larger quantities of pure material will probably make crystal growing easier.

The crystal structures of methyl-β-glucoside $\cdot$ $1/2H_2O$, methyl-β-cellobisoide $\cdot$ H_2O, D-galacturonic acid $\cdot$ H_2O, and β-D-mannose are amenable to solution by x-ray diffraction techniques.

RECOMMENDATIONS

Greater quantities of pure cellodextrins are currently being prepared by N. Povey in his thesis research. When these are available, suitable crystal preparation of the cellodextrins should then be attempted.

The crystal structure determinations of methyl-β-glucoside, methyl-β-cellobioside, D-galacturonic acid, and β-D-mannose would each contribute significantly to our knowledge of sugar structures and ultimately, to the structure of polysaccharides such as cellulose and hemicelluloses. The problems could be approached by attempting to apply current structure knowledge to the solution. This technique will be exceedingly helpful in the structure determination of polysaccharides. These structure problems would make good Ph.D. theses research for the right students and every effort will be made to encourage student interest. Otherwise, this work will be proposed for Institute or other support.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Miss Charlotte Meredith who carried out all of the experimental work except for that on methyl-β-cellobisoide and to Mr. Delbert Schuster who determined the density of methyl-β-cellobioside.

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PROJECT REPORT FORM

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PROJECT NO. 1102-8
COOPERATOR Institute of Paper Chemist
REPORT NO. 20
DATE July 12, 1967
NOTE BOOK 1109
PAGE 45 TO 52
SIGNED George Lauterbach
George E. Lauterbach

QUATERNARY SURFACTANTS AS RETENTION AIDS FOR STARCH XANTHIDE

AN EXPLORATORY EXPERIMENT

SUMMARY

An exploratory experiment has confirmed the belief that a small amount of quarternary surfactant would enhance sorption of starch xanthide by papermaking fibers. Octadecylamine acetate (2.5 g. per 100 g. xanthide starch) is more effective at 25°C. as a retention aid for starch xanthide on fines-free bleached kraft fiber than .0002 N alum (9% on fiber weight). Previously, alum was essential for retaining starch xanthide in handsheets. Alum is effective for this purpose only in acid media. Similar surfactants have been effective retention aids for cornstarch at pH 9. By analogy it should be possible to treat paper effectively with starch xanthide in alkaline systems.

INTRODUCTION

This report describes an exploratory study of a way to improve the retention of starch xanthide in handsheets. The specific combination of materials and conditions is related to Project 2580, 2541, and 2615, but is sufficiently different to warrant an evaluation separately.

The performance of pearl cornstarch as a beater adhesive is enhanced by the addition of small amounts of quarternary surfactants (1).

Since starch xanthide (oxidatively cross-linked starch xanthate) does retain the ability of the parent starch to form the blue colored complex with iodine and potassium iodide, it was felt that it should also be able to complex with fatty materials such as the quaternary surfactants. The information available to us indicates that complex formation is involved in some way with the improved performance of corn starch.

If starch xanthide-quarternary surfactant complexes are formed then two advantages might be anticipated. One, of course, is the positive charge imparted by the quaternary ammonium group should reduce the energy barrier separating the fiber surface and the xanthide particle. The second advantage could be the stabilization of starch xanthide preparations so that coagulation is reduced. Coagulation or aggregation of the xanthide with itself appears to reduce its effectiveness (2). Only the aspect of improved retention is evaluated at this time.

EXPERIMENTAL

DESIGN OF EXPERIMENT:

Set No.	Alum	Amine
I	+	0
II	+	+
III	0	+

OCTADECYLAMINE ACETATE STOCK SOLUTION

n-Octadecylamine (12.802 g. .0482 moles) was dissolved in warm deionized water containing about 10% more than an equivalent amount of acetic

acid, cooled and made up to 1,000 liters. This use of this amine and the quantity used is based on data obtained under Project 2615.

STARCH XANTHIDE

Starch xanthide was prepared separately from the paper fibers (ex situ) from starch xanthate provided by the U.S.D.A. for Project 2580. The xanthate (26.59 g. Run No. 510, 9.4 g. starch per 100 g. solution) was diluted with 1470 ml. deionized water in a 2-quart fruit jar and brought to 20.0°C. in a water bath. A magnetic stirrer, driven from underneath the water bath, was used to mix the solution. Twenty per cent acetic acid was added to give a pH of 5.3 to 5.4. During the five-minute interval after acidification, 5 ml. of 5% (w/v) potassium iodide was added to the solution. The xanthide was formed by titrating the solution with acidified 1% sodium hypochlorite (1 volume of Hi-lex diluted to 4 volumes, acidified with acetic acid to pH 5.0 to 5.5, and then made up to 5 volumes) to the blue endpoint produced by iodine and starch. Octadecylamine acetate (4.00 g. stock solution) was added at this point. The opalescent preparation was diluted to 2000 ml. (0.125% starch w/v) and returned to the 20°C. water bath. Separate xanthide preparations were made for each sorption condition.

PREPARATION OF THE FIBER SUSPENSION

Fines-free Rayonier bleached kraft fiber beaten to 700 S.-R. before classifying and dewatering (17.14 g. dry basis) was resuspended in 2 l. deionized water in a British disintegrator (300 counts) and diluted to 10.00 liters. When alum was used, 15.2 ml. of 10% solution (w/v) was added at this point. This produces .0002 M alum in the sorption media after the xanthide and fiber

are combined. Fourteen hundred-milliliter portions of the fiber suspension were placed in two-quart fruit jars and equilibrated to 25.7°C. in a water bath.

COMBINING XANTHIDE AND FIBER

Fifteen minutes after the cross-linking reaction was completed, 200-ml. portions of the opalescent starch xanthide preparation were added to the fiber suspensions. The materials were blended by manual shaking for the short exposures (15, 30, and 60 sec.) or by mechanical stirrers for the longer contact periods (4, 16, and 32 minutes). The last three jars of fiber and xanthide were returned to a 25.0°C. water bath. (200 ml. at 20°C. blended with 1400 ml. at 25.7°C. equals 1600 ml. at 25.0°C.) At the end of the specified contact period the fruit jars were dumped into the Noble and Wood sheet mold (8 liters deionized water in deckle box) as the valve was tripped. The deckle box emptied in about six seconds.

The handsheets were couched onto a blotter but were not pressed. Drying was done between blotters for three minutes on a steam drum, couch blotter up. This interval leaves the sheet and blotter damp enough for the sheet to be removed easily and dried on the steam drum for three more minutes. (This procedure avoids having the handsheet and blotter become inseparable at higher xanthide retentions.)

The order of making the sheets is shown below:

Order of Operation	Xanthide Addition	Sorption Termination
1	15 sec.	15 sec.
2	30 sec.	30 sec.
3	32 min.	60 sec.
4	16 min.	4 min.
5	4 min.	16 min.
6	60 sec.	32 min.

This sequence introduces the xanthide into all of the samples within about 8 minutes. The age of the xanthide preparation thus is from 15 to 23 minutes when it is mixed with the fiber. The experimental conditions are summarized in Table I.

TESTING PROGRAM

The single handsheets prepared for each condition and sorption time were tested for wet tensile strength and starch xanthide content according to the procedures being used for Project 2580.

TESTING DATA

The results of the testing program are shown in Table II.

DISCUSSION

Adding a small amount (2.5%) of the quaternary surfactant octadecylamine acetate to starch xanthide immediately after cross-linking, improves xanthide sorption by bleached kraft fibers over that obtained in 0.0002 M alum. Wet tensile strength is similarly improved. It appears that using the surfactant and alum together lowers sorption over that obtained with the surfactant alone. However, this effect is small and needs verification. The effectiveness of the starch xanthide is reduced by using alum and surfactant together. This is shown in the last column of Table II. The wet tensile strength developed per gram of xanthide in the handsheet is lower for the combination of retention aids than for either by itself. The

data for alum and surfactant alone appear to be similar, yet different than those for combination of retention aids.

In Figure 1, xanthide sorption is a linear function of the logarithm of the sorption time. This is consistent with previous experience (3).

Figure 2 is a double log plot of the sorption rate against time. An infinite initial sorption rate would be predicted for all three conditions on the basis of the apparent linearity of the curves.

The finding that a quaternary surfactant improves retention of starch xanthide is important. Previously, the use of starch xanthide was limited to applications compatible with alum. The fact that starch xanthide responds to long chain fatty amine salts similarly to the parent starch suggests that xanthide may be used effectively in alkaline systems at least as high as pH 9 (4).

FUTURE WORK

In addition to determining the effective pH range for fatty amine salts as retention aids for starch xanthide, the effect of these materials upon the cross-linking reaction should be examined. It is possible that cross-linking (to produce xanthide from xanthate) in the presence of the surfactant could produce a more stable xanthide preparation. This might allow cross-linking at higher concentrations (i.e., higher than 0.17%) or extend the usable life of the xanthide preparation.

TABLE I

SUMMARY OF EXPERIMENTAL CONDITIONS

		I	II	III
Alum Concentration:				
	Molar	2×10^{-4}	2×10^{-4}	0
	g/100 g. fiber	8.9	8.9	0
Octadecylamine Acetate:				
	g/100 g. xanthide starch	0	2.5	2.5
	mole/100 mole A.G.U.	0	1.26	1.26
Xanthide Starch:				
	g/100 g. fiber	10.42	10.42	10.42
Fiber + Alum	pH	4.2	--	6.8
Dilute Xanthate	pH	10.6	10.6	10.6
Acidified Xanthate:	pH	5.3	5.4	5.3
20% HOAc used	ml	2.2	2.2	2.2
1% HOCl (acidified Hi-lex) added,	ml	17.3	19.5	18.8
Xanthide Preparation (1500 ml.)	pH	4.9	5.0	4.9
Xanthide plus Amine Acetate	pH	--	5.0	4.9
Xanthide plus Acetate (2000 ml.)	pH	--	5.1	5.1
Xanthide Preparation After 13 min.	pH	4.9	5.1	5.1

TABLE II

EFFECT OF QUATERNARY SURFACTANT

Run No.	Contact Time, min	.0002 M Alum	2.5% C_{18}-amine Acetate	Instron Wet Tensile[a], lb/in. (2)	Δ Wet Tensile[b]	Glucan, % (2)	Xanthide, g/100 g. sheet	Xanthide, g/100 g. fiber	Retention Efficiency, %	Retention Rate, g/100 g. ÷ min.	Δ Tensile Rate, lb/in/min.	Δ Tensile ÷ Xanthide, lb/in ÷ g/100 g.
I	1/4	+	0	0.92	.49	6.06	0	0	0	--	1.96	--
	1/2			1.08	.55	6.44	0.38	0.38	3.7	.76	1.05	1.45
	1			1.56	1.13	6.94	0.86	0.89	8.5	.89	1.13	1.27
	4			1.96	1.53	7.33	1.27	1.29	12.4	.32	.38	1.19
	16			2.48	2.05	7.76	1.70	1.73	16.6	.11	.13	1.19
	32			2.54	2.11	8.06	2.00	2.04	19.5	.064	.067	1.03
II	Blank	+	+	0.38	--	6.12	--	--	--	--	--	--
	1/4			1.53	1.10	7.10	1.04	1.05	10.1	4.2	4.4	1.04
	1/2			1.79	1.36	7.44	1.38	1.40	13.4	2.8	2.7	.97
	1			2.32	1.89	8.11	2.05	2.09	20.1	2.1	1.9	.91
	4			2.88	2.45	8.72	2.66	2.73	26.2	.68	.61	.90
	16			3.83	3.40	9.63	3.57	3.70	35.5	.24	.21	.92
	32			3.41	2.98	10.18	4.12	4.30	41.3	.134	.093	.69
III	Blank	0	+	0.48	--	6.00	--	--	--	--	--	--
	1/4			2.10	1.67	7.28	1.22	1.24	11.9	5.0	6.7	1.34
	1/2			2.42	1.99	7.76	1.70	1.73	16.6	3.46	4.0	1.15
	1			2.80	2.37	8.12	2.06	2.10	20.2	2.10	2.4	1.18
	4			3.71	3.28	8.84	2.78	2.86	27.4	.71	.82	1.15
	16			3.85	3.42	10.59	4.53	4.74	45.5	.283	.21	.72
	32			3.32	2.89	11.04	4.98	5.24	50.3	.164	.090	.57

[a] Samples soaked overnight at 73°F.

[b] Sample - Blank, i.e., $\frac{38 + .48}{2}$

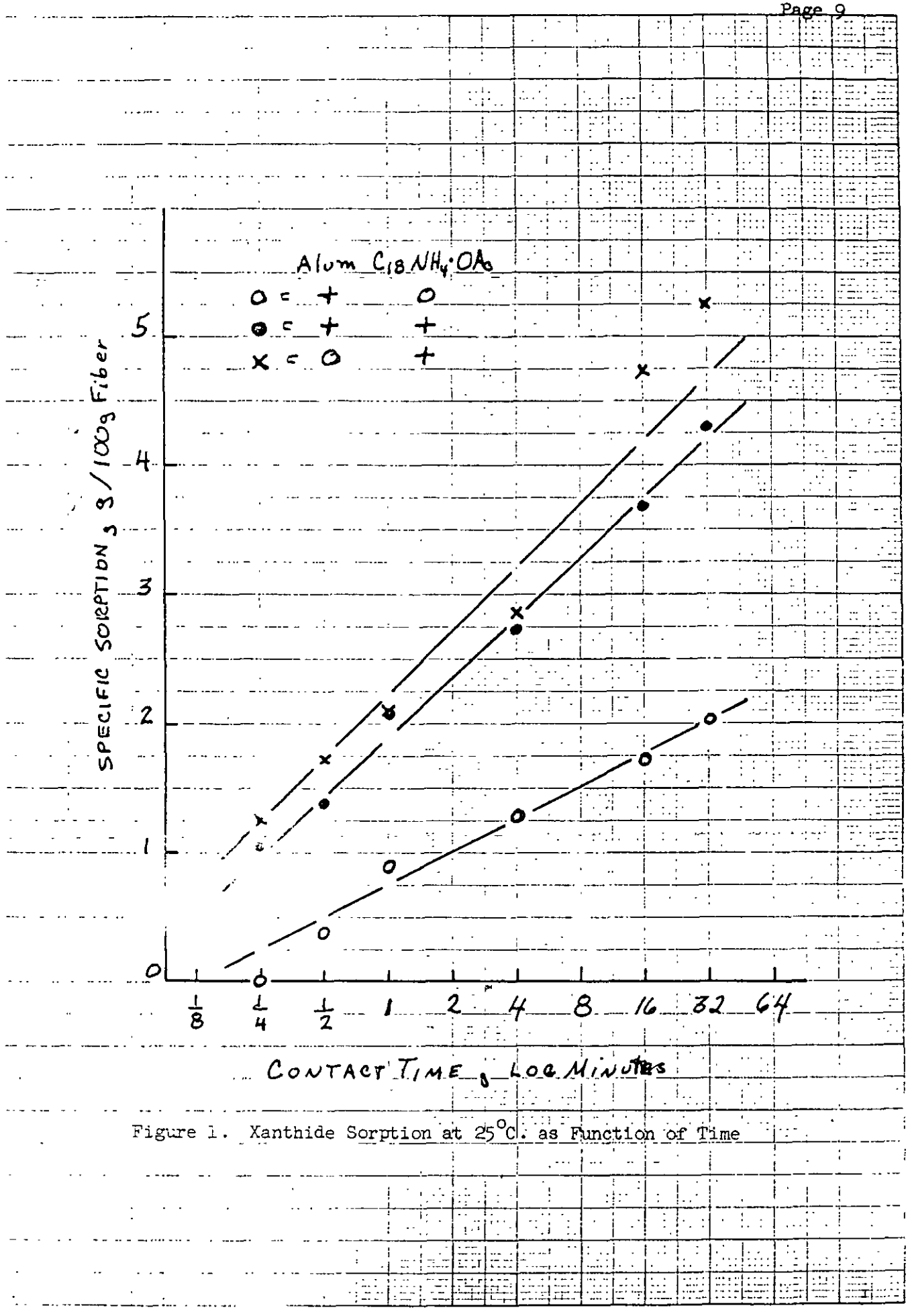

Figure 1. Xanthide Sorption at 25°C. as Function of Time

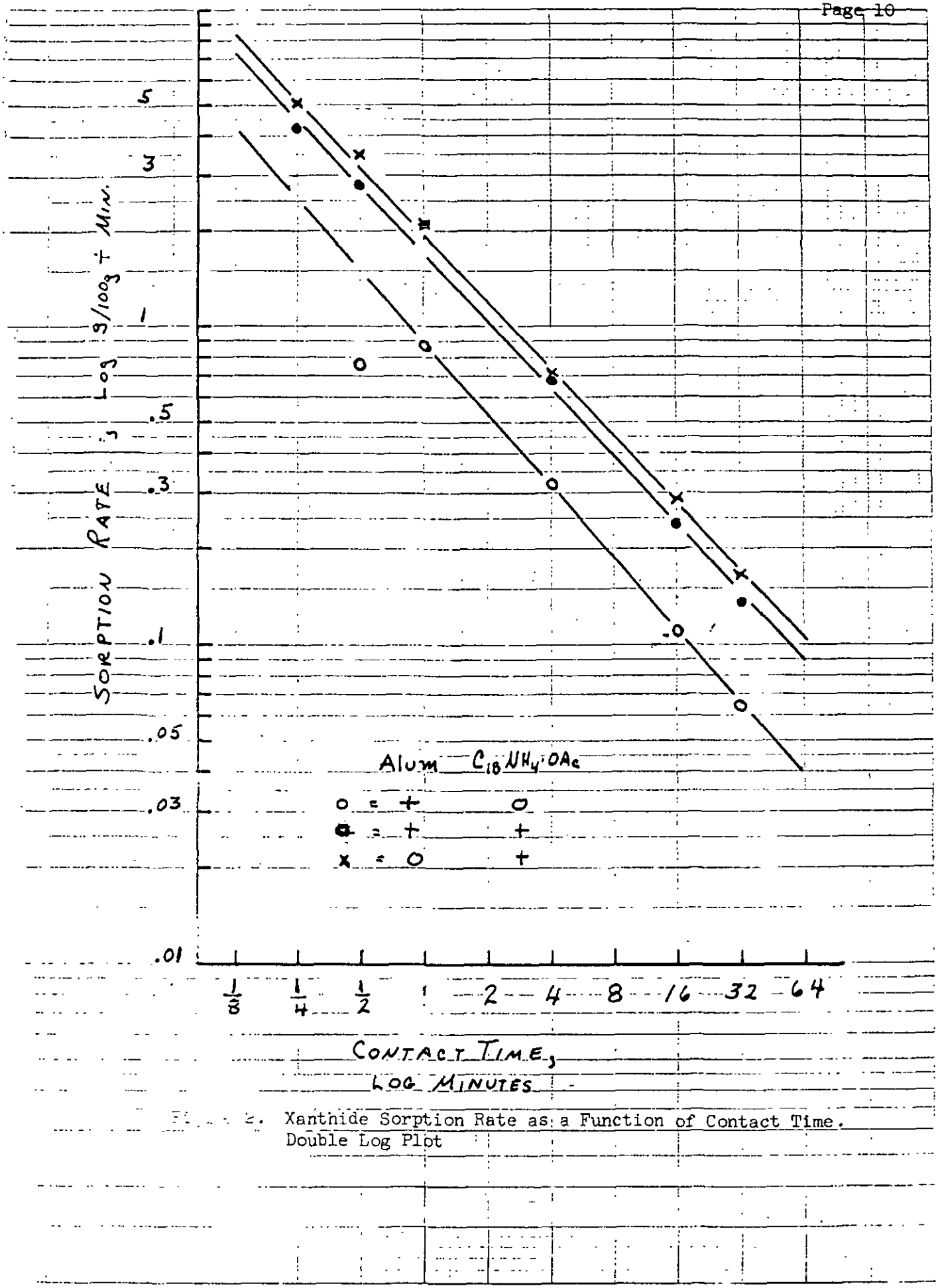

Fig. 2. Xanthide Sorption Rate as a Function of Contact Time. Double Log Plot

LITERATURE CITED

1. Project 2541, The Institute of Paper Chemistry, Reports Two and Three.

2. Project 2580, The Institute of Paper Chemistry, Report Seven, p. 12-27.

3. Project 2580, The Institute of Paper Chemistry, Report Six, p. 21.

4. Project 2541, The Institute of Paper Chemistry, Report Three, p. 18-20.